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6. AUTHOR(S)
Barry E. Cole
R.H. Horning

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)
Honeywell Technology Center
Plymouth, MN 55441

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13. ABSTRACT *(Maximum 200 words)*

Collosal magnetoresistive (CMR) films, on lattice matched substrates, can achieve a thermal coefficient of resistance (TCR) in excess of 10%, significantly higher than the present 2% VOx. This material is not a pyroelectric but was an extension of the existing resistive bolometer approach. The resistance change which has been much studied arises from electron transport changes with temperature caused by changes in the electronic energy levels of the ferromagnetically coupled electron at different crystal sites and is a function of the composition. Lattice-matched substrates of LaAlO3 and, to a somewhat lesser degree, YSZ are excellent for growth of this material. It became apparent that an oriented film of YSZ would benefit both PbTiO3 growth and colossal magnetoresistive (CMR) film growth in the Honeywell DARPA AIM program since both detector films were similar perovskite type films where crystal growth and orientation are critical to achieving the desired properties. In 1997, this program was redirected from its initial focus on a sacrificial layer to support PbTiO3 growth to focus on the development of a YSZ buffer film for oriented growth of CMR films both in plane and out of plane.This program has resulted in the development of a process for the deposition of YSZ films with both out-of-plane and in-plane orientation on the fundamental pixel material, silicon nitride. The YSZ material technology developed in this program, has been used in the AIM program, to provide the necessary growth habitat for CMR thin films resistors. These resistors have achieved TCRs of 3.5% on silicon nitride.

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Development of a Two-Level Fabrication Process for PbTiO3 Pyroelectric Arrays

Final Report

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Prepared by

Honeywell Technology Center
12001 Highway 55
Plymouth, MN 55441

for

Department of the Army
Army Research Office
4300 South Miami Blvd.
Research Triangle Park, NC 27709-2211

Barry Cole
Dr. Barry E. Cole
Principal Investigator

Mr. Earl Benser
Microsensors Section Head

Abstract

Phase II of the ARO Program started as continuation of the development of $PbTiO_3$ pyroelectric detector pixels. In this activity, Honeywell had demonstrated a process for the deposition of thin film $PbTiO_3$ by using a dual target ion beam sputtering process. The work in Phase I, showed that it was significantly easier to deposit high quality lattice matched $PbTiO_3$ films on lattice matched substrates, most noticeably MgO. It was significantly more difficult to achieve good pyroelectric properties on Si_3N_4 and to that extent work began on the development of a buffer layer, most noticeably MgO. The purpose of Phase III, was to develop a novel process in which $PbTiO_3$ films were grown on a sacrificial layer of MgO. Although it was fairly easy to deposit MgO, the crystalline quality of the material was never good. The use of several different metals to buffer the growth of the MgO proved of little help in the early work. At this early point in time in Phase II of the ARO program, Honeywell was awarded a program, AIM, to develop a bolometer using colossal magnetoresistive (CMR) films such as LaCaPbMnO on Si_3N_4 substrates. This CMR material is not a pyroelectric, like $PbTiO_3$, but is a potential replacement for the existing VOx resistor in uncooled bolometer array design (Figure 1). This CMR material, on lattice matched substrates, can achieve a thermal coefficient of resistance (TCR) in excess of 10%, significantly higher than the present 2% VOx resistor material used in the present uncooled bolometer arrays which at present have achieved LWIR sensitivities of about 20 mKelvin. Figure 2 compares the TCRs of a number of materials and shows the unique properties of these CMR films. The resistance change which has been much studied arises from electron transport changes with temperature caused by changes in the electronic energy levels of the ferromagnetically coupled electron at different crystal sites and is a function of the composition as shown in Figure 3. Lattice-matched substrates of $LaAlO_3$ and, to a somewhat lesser degree, YSZ are excellent for growth of this material. It became apparent that an oriented film of YSZ would benefit

both $PbTiO_3$ growth and colossal magnetoresistive (CMR) film growth in the Honeywell DARPA AIM program since both detector films were similar perovskite type films where crystal growth and orientation are critical to achieving the desired properties. In 1997, this program was redirected to focus on the development of a YSZ buffer film with both in-plane and out-of-plane oriented growth.

This program has resulted in the development of a process for the deposition of oriented YSZ films on the fundamental pixel material, amorphous silicon nitride. The YSZ thin film deposition technology developed in this program, has subsequently been used in the AIM program, to provide the necessary growth habitat for CMR thin films resistors. These resistors have achieved TCRs of 3.5% on silicon nitride. Work is continuing in the AIM program to further refine and improve the YSZ process initially demonstrated in this effort.

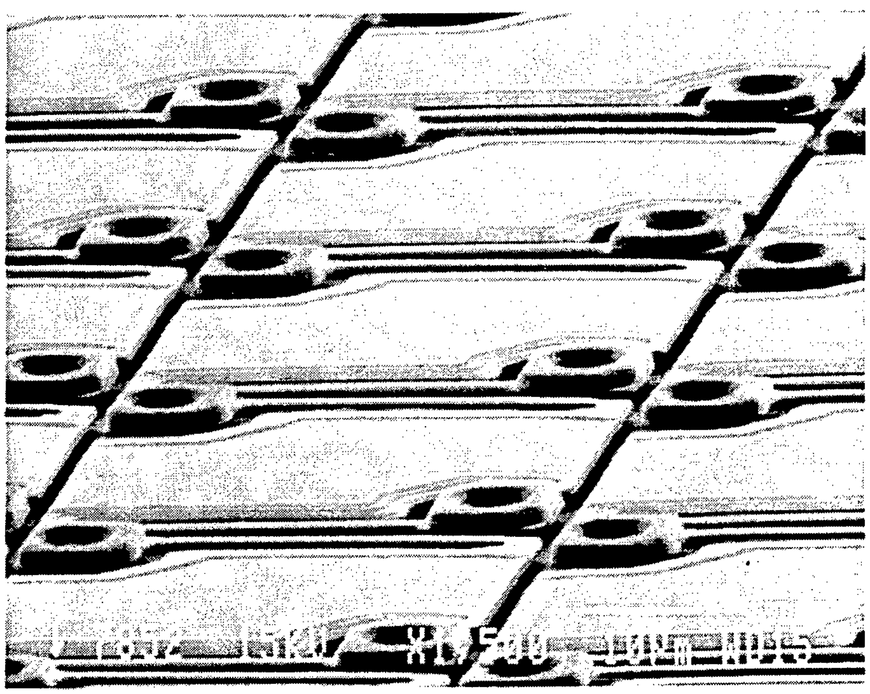


Figure 1: SEM micrograph of pixels in present uncooled microbolometer array

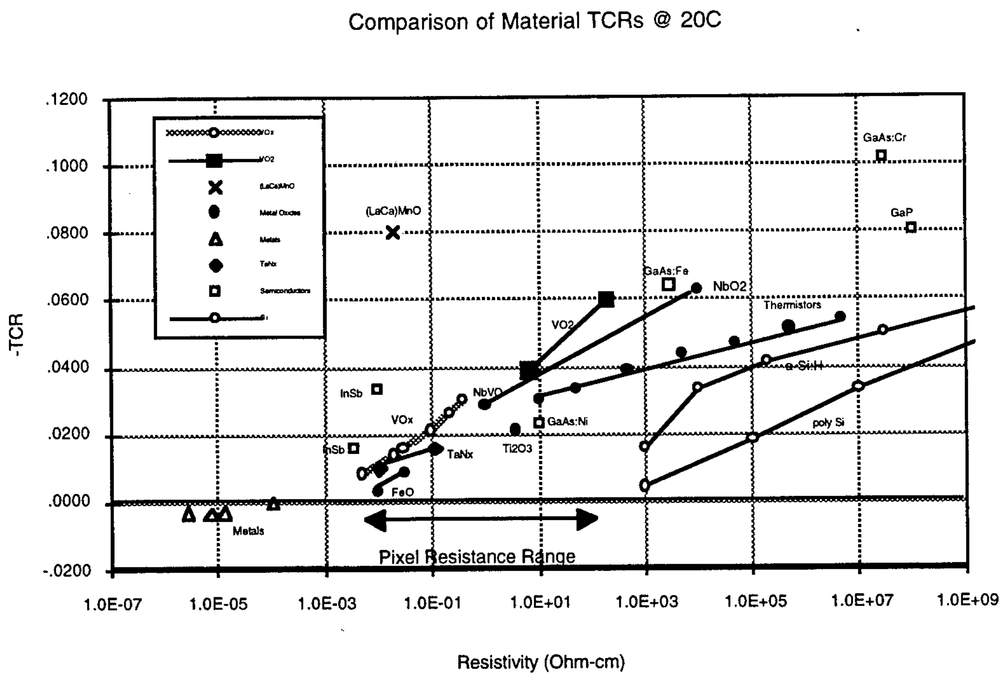


Figure 2: Comparison of film resistance and TCRs for a range of materials showing the unique properties of LaCaMnO films

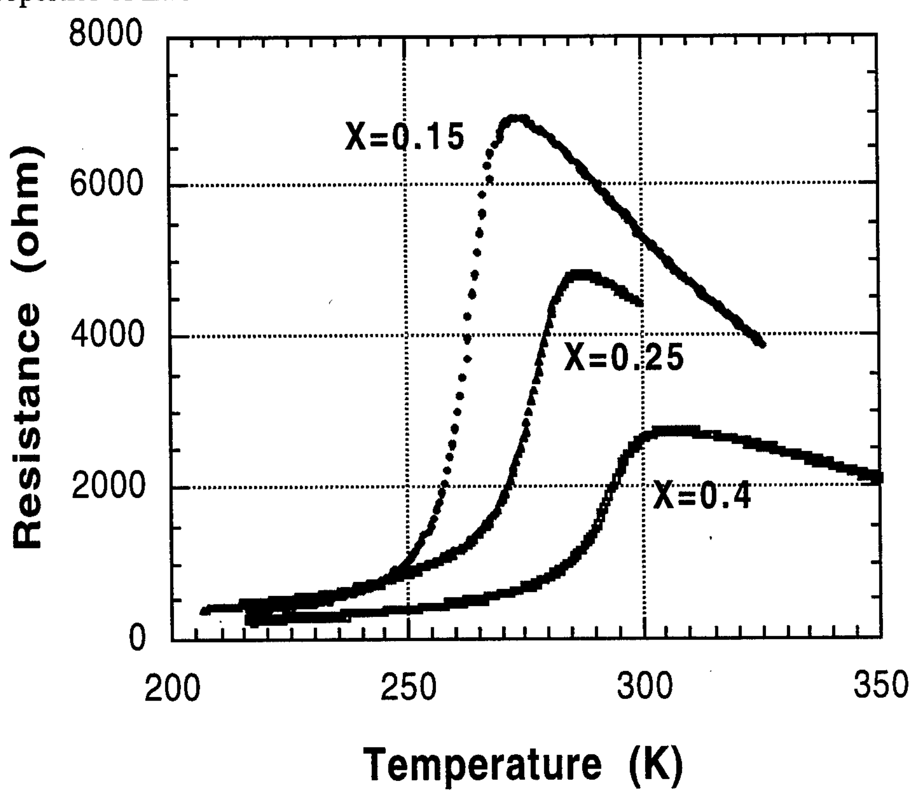


Figure 3: Variation of transition, TCR, and resistance with stoichiometry of $La_xCa_{1-x}MnO_3$ film

Importance of YSZ Growth

The performance of a microbolometer array comparable to the present array with the exception of the addition of CMR films was calculated for the present measured CMR thin film 1/f noise K value of 2×10^{-13} for a range of TCRs. In part, this calculation was intended to estimate the expected bolometer performance with these measured noise values. The other purpose of this analysis was to quantify the performance benefits of TCR. It can be seen that the performance continues to improve with greater TCR significantly up to TCR values of about 10% which provides a 4x improvement over the present VOx material.

Pixel Properties

Pitch = 51 um
Size = 240x340
IR = 8-12 um
Frame Rate = 30 Hz
Absorptance = 80%
Fill Factor = 50%
R = 20KOhms
T = 300K
C = 3e-9 J/K
G = 1.5e-7
tau = 20 msec
F2 = 15 Khz
f1 = .001 Hz
K = 2e-13
dT = 2K

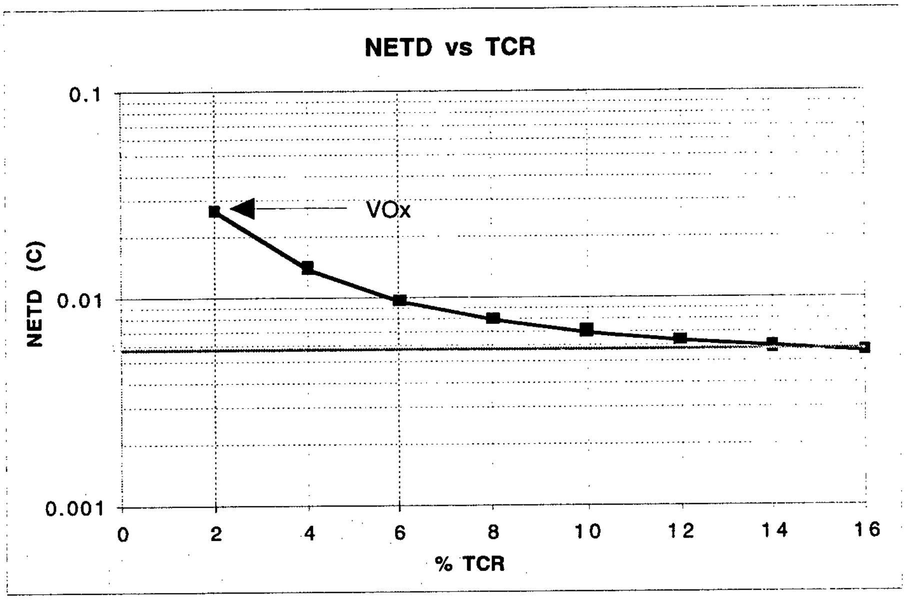
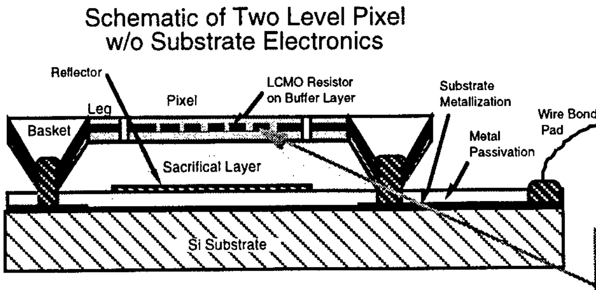


Figure 4: Calculated performance of bolometer pixel with CMR thin films.

Figure 5 shows a schematic of the complete process for bolometer formation, a significant number of the actual process steps. A key element of this process is the need to have thin film YSZ as a buffer film on the pixel supporting CMR material growth. Figure 6 is a micrograph of a patterned CMR serpentine resistor on a bulk YSZ substrate containing 122 squares and representative of the resistor that would be formed on a pixel except for the use of bulk YSZ rather than a thin film YSZ buffer layer.



Approximate Process Steps

1 Deposit substrate metal on Si3N4 coated Si
2 Pattern metal
3 Passivate and planarize metal with SiO2 films
4 Deposit and pattern reflector
5 Deposit sacrifical layer
6 Form basket vias to metal contacts
7 Deposit bottom Si3N4 and YSZ buffer film
8 Deposit CMR and buffer films at NZAT
9 Pattern pattern detector films
10 Deposit protect Si3N4
11 Etch via to detector film
12 Deposit and pattern ohmic metal (legs)
13 Deposit top bridge nitride
14 Etch Si3N4 in via and deposit plug metal
15 Pattern thermal structure
16 Etch sacrificial layer
17 Dice wafer and mount in package

Present Process Steps: @ NZAT @ HI

Figure 5: Approximate pixel and resistor processing steps.

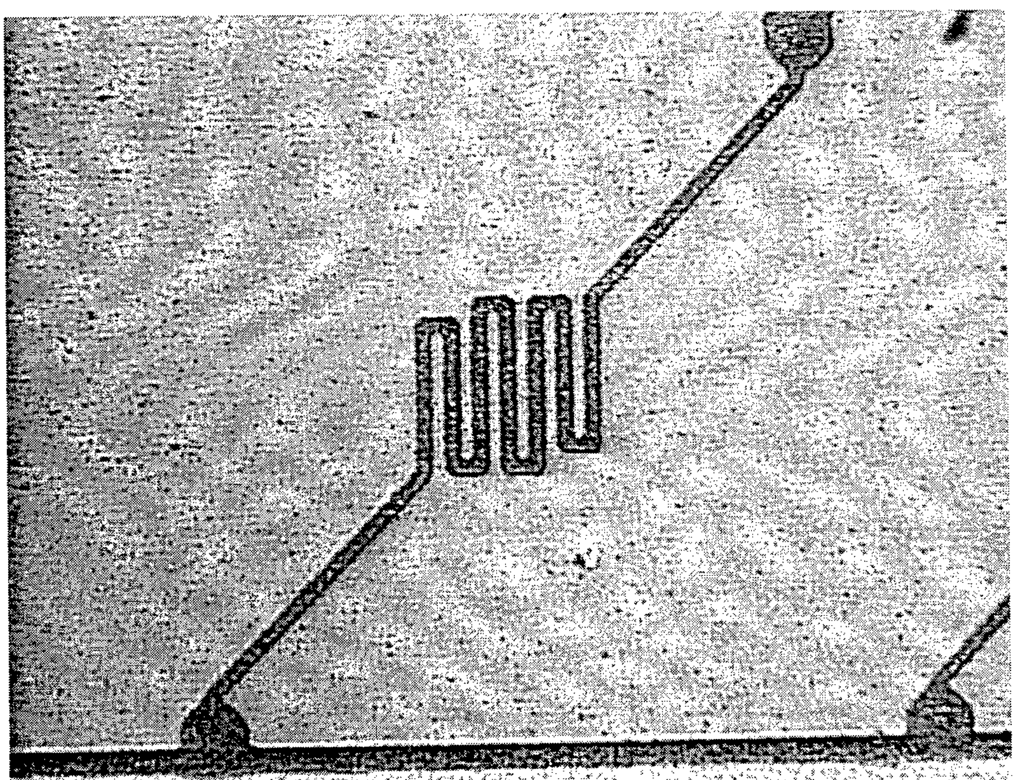


Figure 6: Patterned serpentine LCMO resistor on single crystal YSZ substrate.

Buffer Film Selection_

CMR materials $(La_{1-x}A_x)MnO_3$ (A: Ca, Ba, Sr, and Pb) have a potential to be used in advanced infrared microbolometers because their superior properties of high TCR and low resistivity. The crystalline nature of the CMR materials requires that they grown on a buffer film which support crystallization. LCMO materials grow very well on lattice matched $LaAlO_3$ substrates because of the only 2% lattice mismatch. YSZ, unlike $LaAlO_3$, can be readily grown in thin film form and can be deposited by usual sputtering techniques. If the LCMO grows along the diagonal of a (100) oriented YSZ crystal, then the lattice mismatch is only 6%. While not good enough for well oriented films, it is sufficiently close to be used in conjunction with another buffer films such as $Bi_3Ti_4O_{12}$, YBCO, or CeO_2 to provide the proper match. LPCMO CMR films deposited on bulk YSZ have crystalline properties as shown in the XRD spectra of Figures 7 and 8. The lattice mismatch between YSZ and LCMO forces the transition to lower temperatures than that achieved on ideally lattice matched $LaAlO_3$ substrates. As can be seen from the XRD spectra of Figure 7, the use of YSZ alone creates LPCMO resistor films with a undesired (110) orientation. The addition to single crystal YSZ of a better lattice matched buffer film, such as YBCO in Figure 5, makes the resistance transition sharper, the TCR higher, and the transition temperature closer to room temperature where operation is desired. The LPCMO film as seen from the XRD spectra of Figure 8 achieves the desired (100) orientation. This demonstration on single crystal YSZ indicates that if crystalline YSZ pixel films could be grown, high TCR pixels are achievable.

Table 1: Properties of lattice matched materials for consideration as buffer layers

Material	Crystal	Relevant Lattice constant	Lattice mismatch
LCMO resistor	Cubic	3.87 (diagonal - 5.47)	
$LaAlO_3$	Cubic	3.792	2.0%
YSZ	Cubic	5.14	6.1%
CeO_2	Cubic	5.41	1.2%
YBaCuO	Orthorhombic	3.82 3.89	1.3%
$Bi_3Ti_4O_{12}$	tetragonal	5.45	0.5%

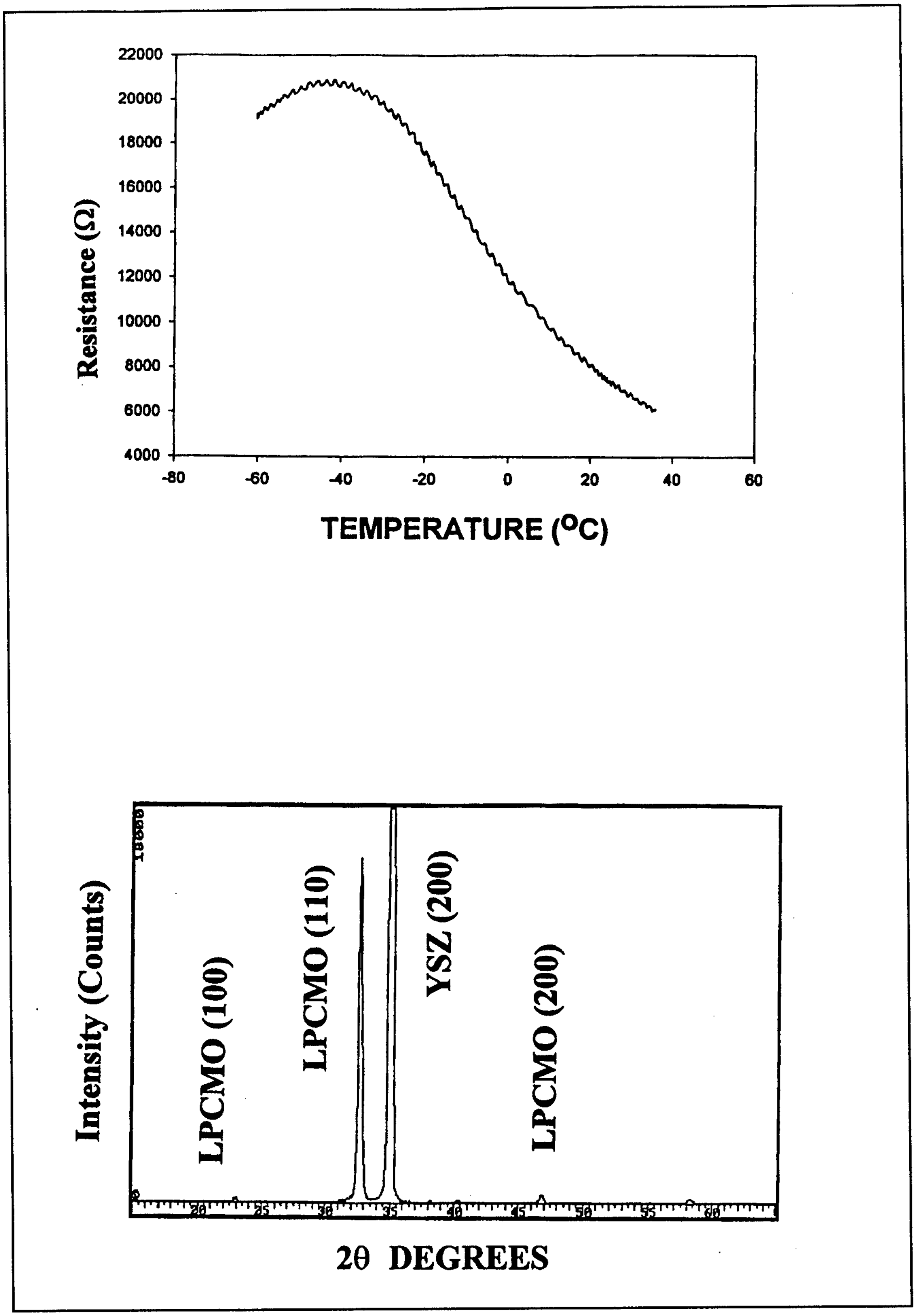


Figure 7: The Θ–2Θ diffraction pattern and R vs T curves measured for LPCMO deposited directly on (100) YSZ single crystal.

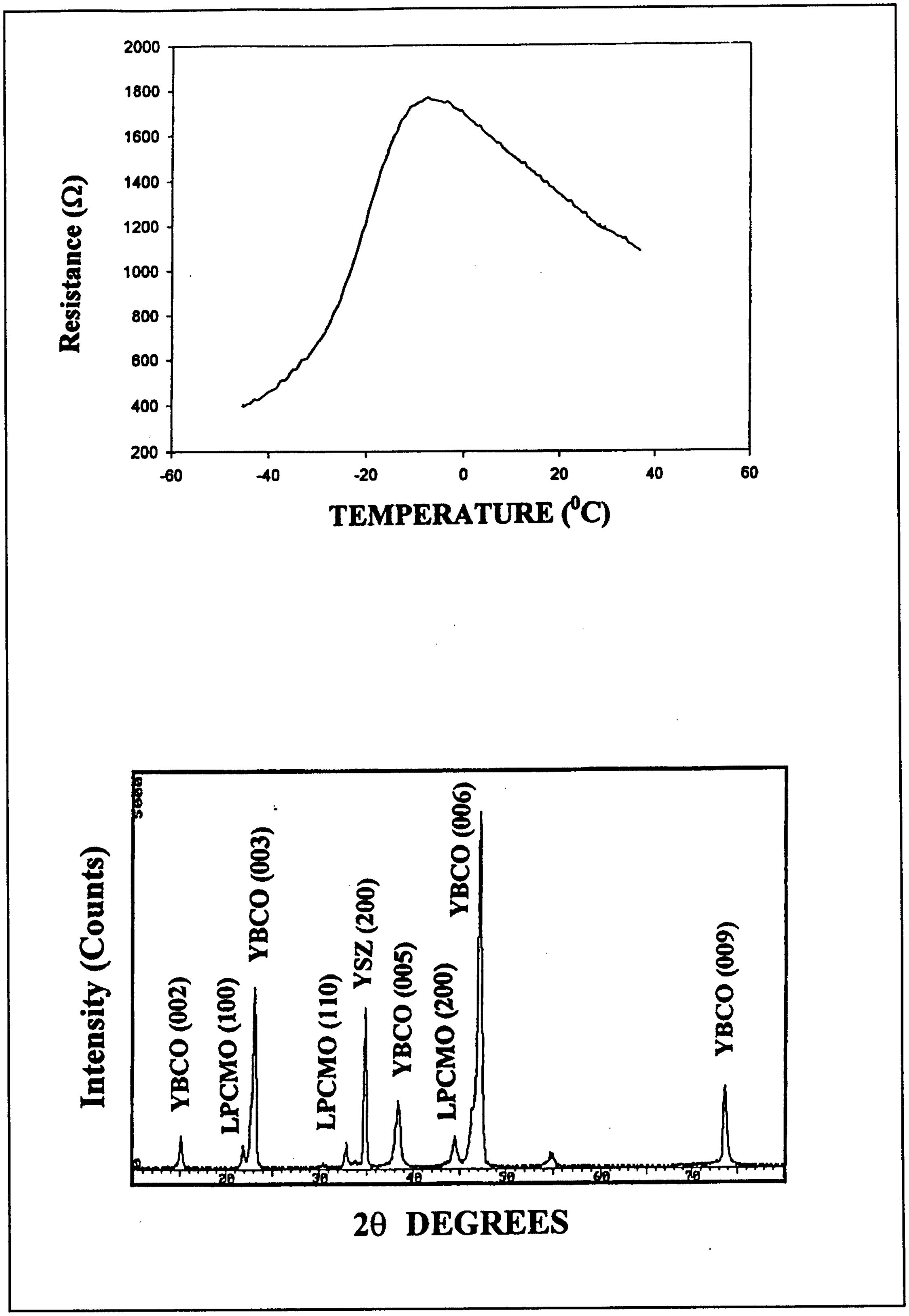


Figure 8: The Θ–2Θ diffraction pattern and R vs T curves measured for LPCMO deposited on (100) YSZ single crystal with an additional YBCO buffer film.

For YSZ to be a successful buffer film, it is important for the YSZ film to be grown with both c axis orientation normal to the film and with in plane alignment of the crystallites. The solution to is to use a report method reported for the deposition of biaxial textured YSZ layer on amorphous films by ion beam assisted deposition technique (IBAD). The IBAD is a method of using a low energy secondary ion beam to irradiate substrate while the first ion beam sputter deposits the material onto the substrate. By providing this second ion beam angle of 54 degrees, the YSZ film will be forced to grow with a (100) orientation rather than the preferred (111). Secondly, the in plane orientation of the a and b axes of the individual polycrystals will be aligned in the direction of the secondary beam. This texturing is call biaxial.

YSZ Buffer Film Development at Honeywell

Having demonstrated that good high TCR CMR films can be grown on bulk (100) oriented YSZ albeit with slightly lower transition temperature than desired, an effort was undertaken in this program to develop the YSZ thin film buffer films. Honeywell developed and demonstrated the previously mentioned IBAD process for high quality biaxial YSZ layers on Si3N4 coated Si wafers for deposition of LPCMO films. To get (100) YSZ, it has been reported by Iijima et al, IEEE Transactions on Applied Superconductivity, Vol. 3, No 1. p.1510-1515 (1993) that the use of a second ion beam aimed at the substrate at approximately 53 degree angle and at 300V beam will promote the growth of (100)-oriented YSZ on Ni-based alloy substrates. A Honeywell dual ion beam system which had a secondary ion gun capable of beam voltages of no more than 100V was first used to explore this process. The XRD results showed that the YSZ crystallinity was low but that the second gun did seem to encourage a stronger (100) orientation over (111). With this suggestion of improvement, a second dedicated Honeywell ion beam system (Figure 9) with a secondary ion gun with better properties than the one first used

was set up. In the second system, the secondary gun parameters were further developed. The angle of the assist beam to the substrate normal, and the relative sputtering and assist currents were modified to explore the range of proper deposition parameters. During the course of this work we have explored the properties of YSZ deposited at a number of different conditions.

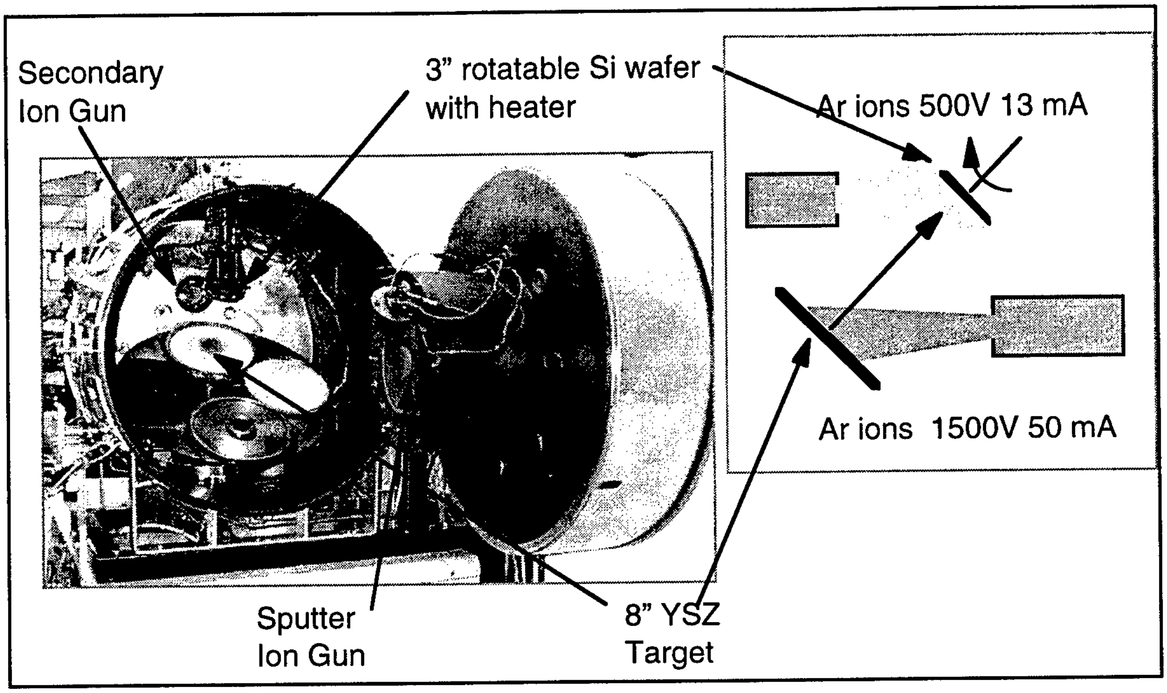


Figure 9 : Honeywell dual gun system for YSZ thin film deposition

Without a second gun or temperature, the YSZ film is amorphous. Without the second gun, YSZ orientation at high deposition temperatures is predominantly (111) on Si3N4 (Figure 10) or a metal buffer film (Figure 11). The use of a second ion gun with the film at elevated temperature still produces a strong (111) orientation (Figure 12). Presumably, the high temperature provides sufficient thermal energy to overcome the secondary beam effects and causes the films to grow with (111) orientation.

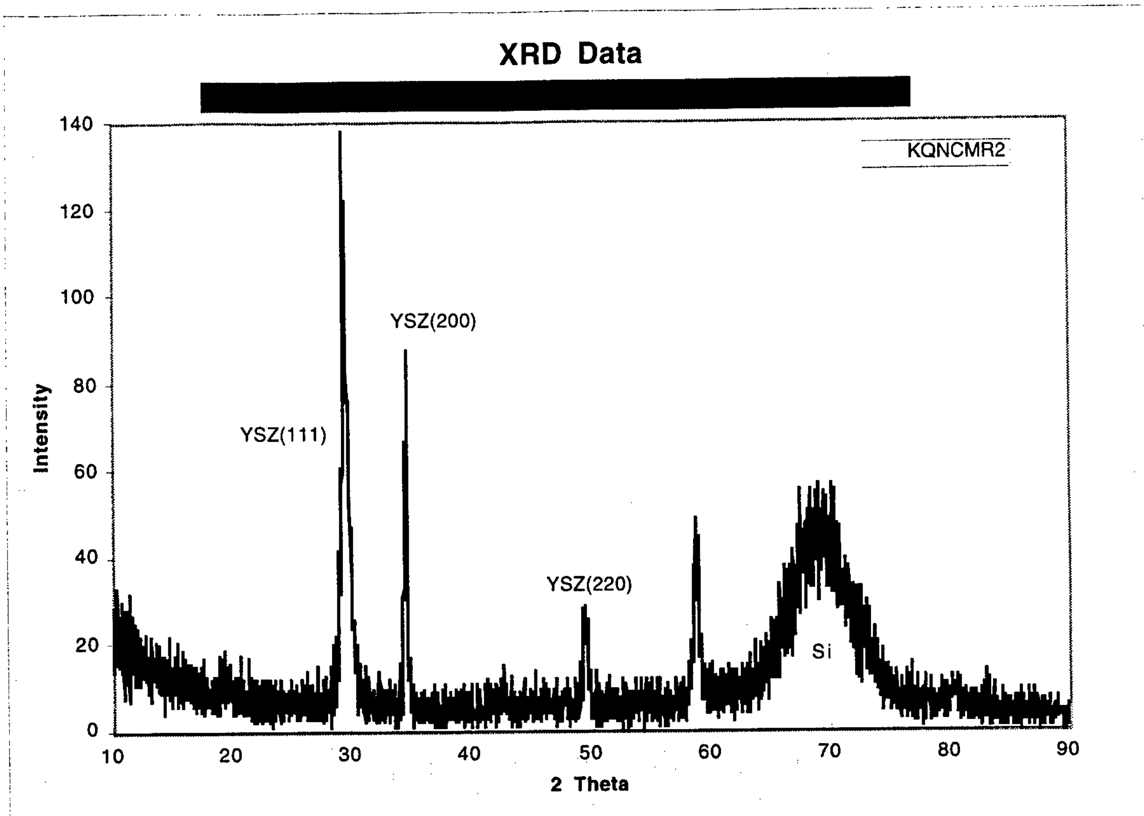


Figure 10: YSZ deposited at high temperature to assist deposition.

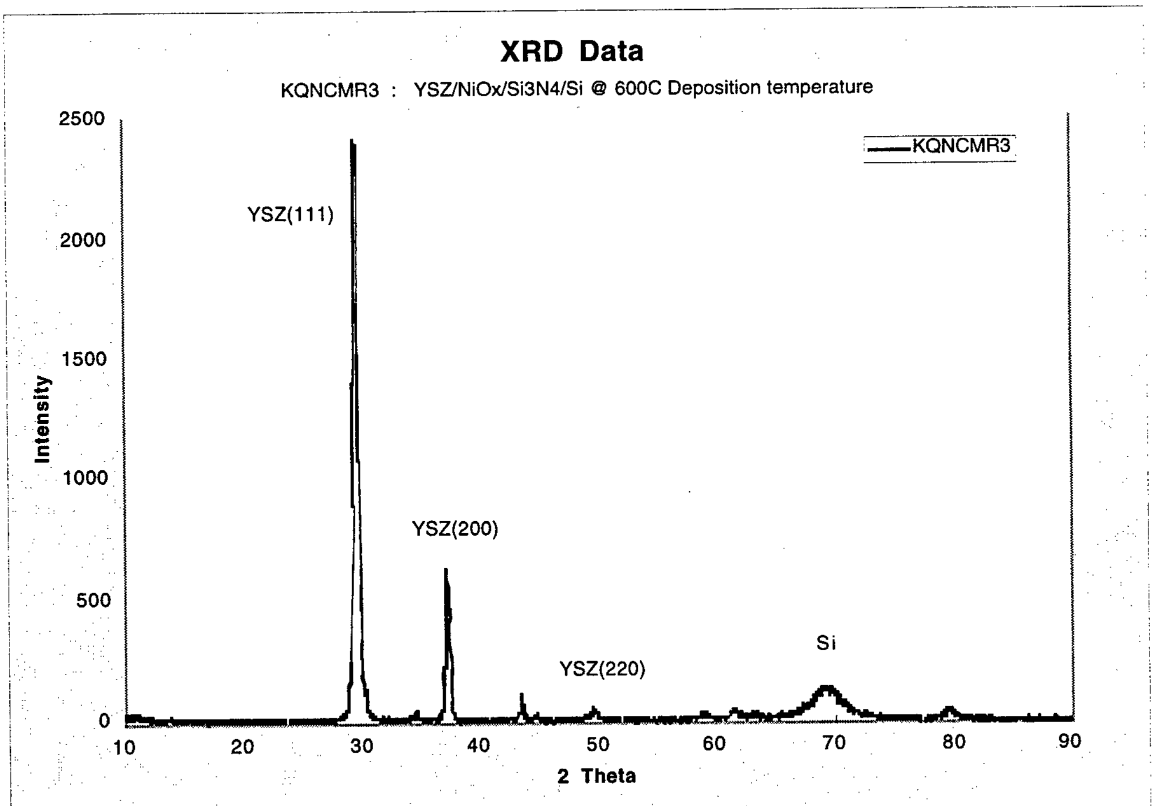


Figure 11: YSZ deposited with a single gun on Ni substrate at high temperature

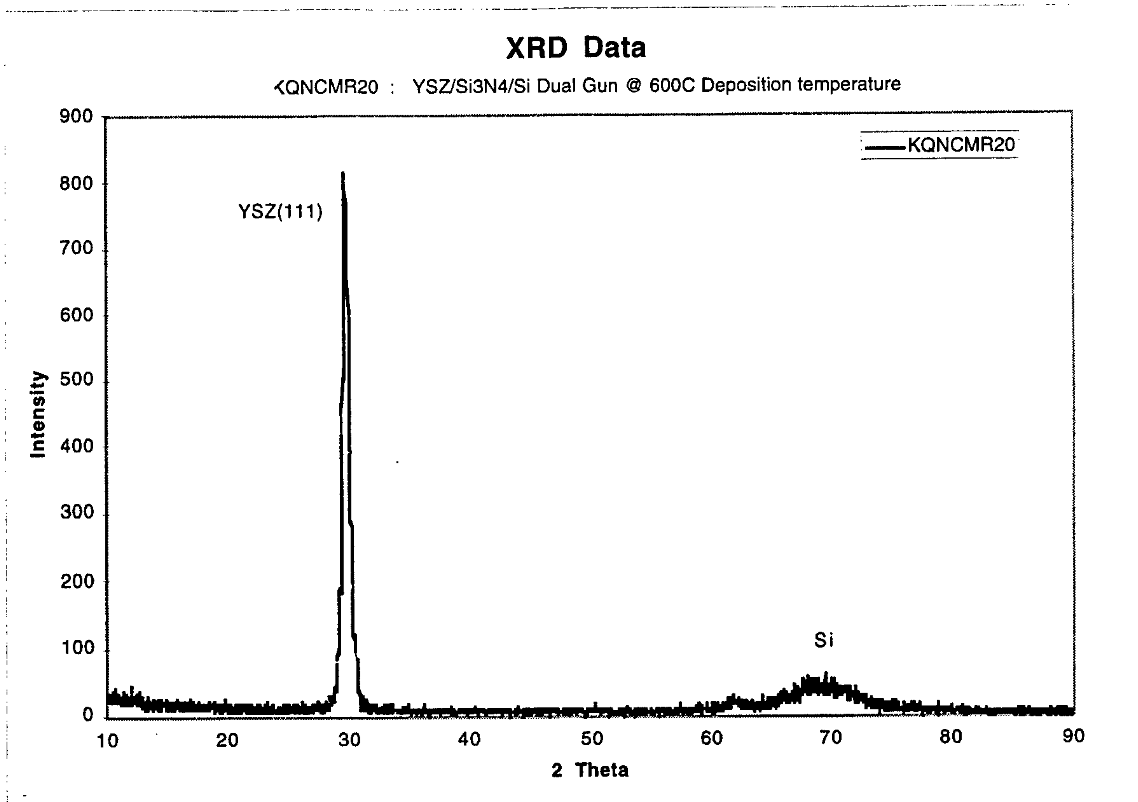


Figure 12: YSZ deposited with dual gun process and high temperature

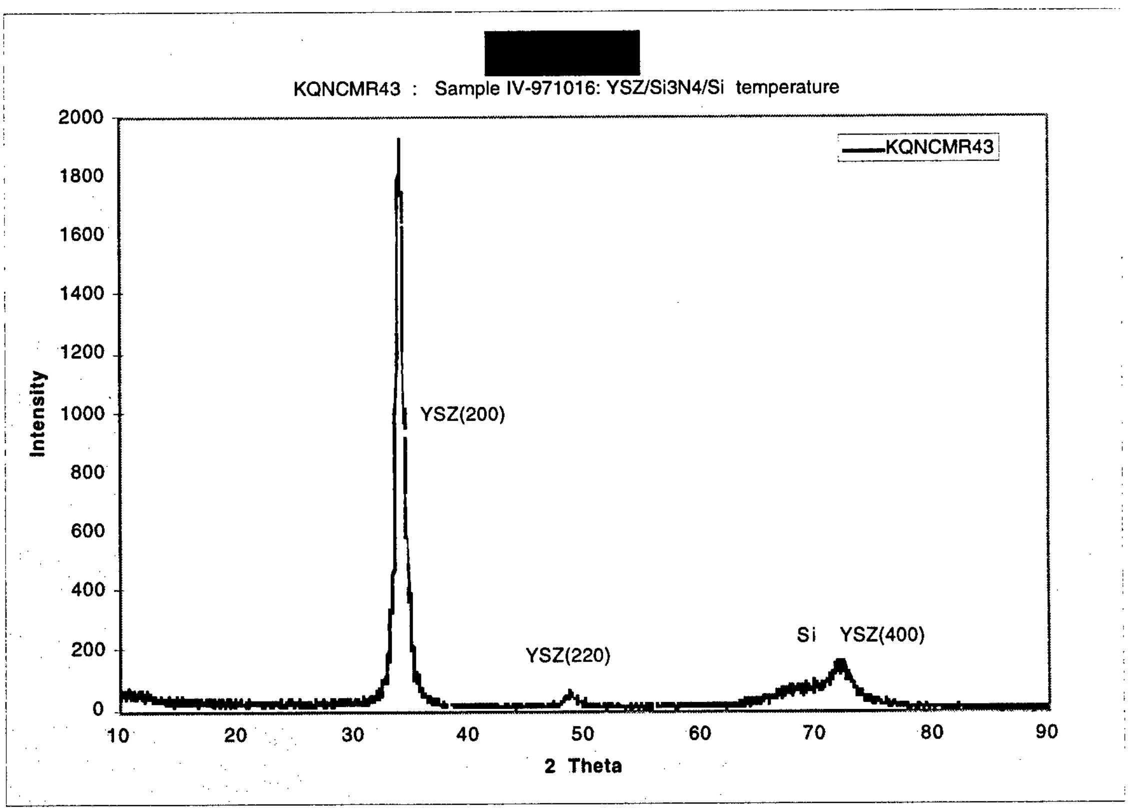


Figure 13: (100) Oriented YSZ film using 2 gun IBAD approach.

With the second gun at the proper current density of approximately 1 mA/ square inch and proper 50 degree angle, the YSZ films are highly (100) oriented when deposited at room temperature as shown in Figure 13.

The oriented films annealed to temperatures as high as 700C in air for 1 hour still maintain and actually have reinforced crystallinity as shown in the XRD spectra of Figure 14 and 15.

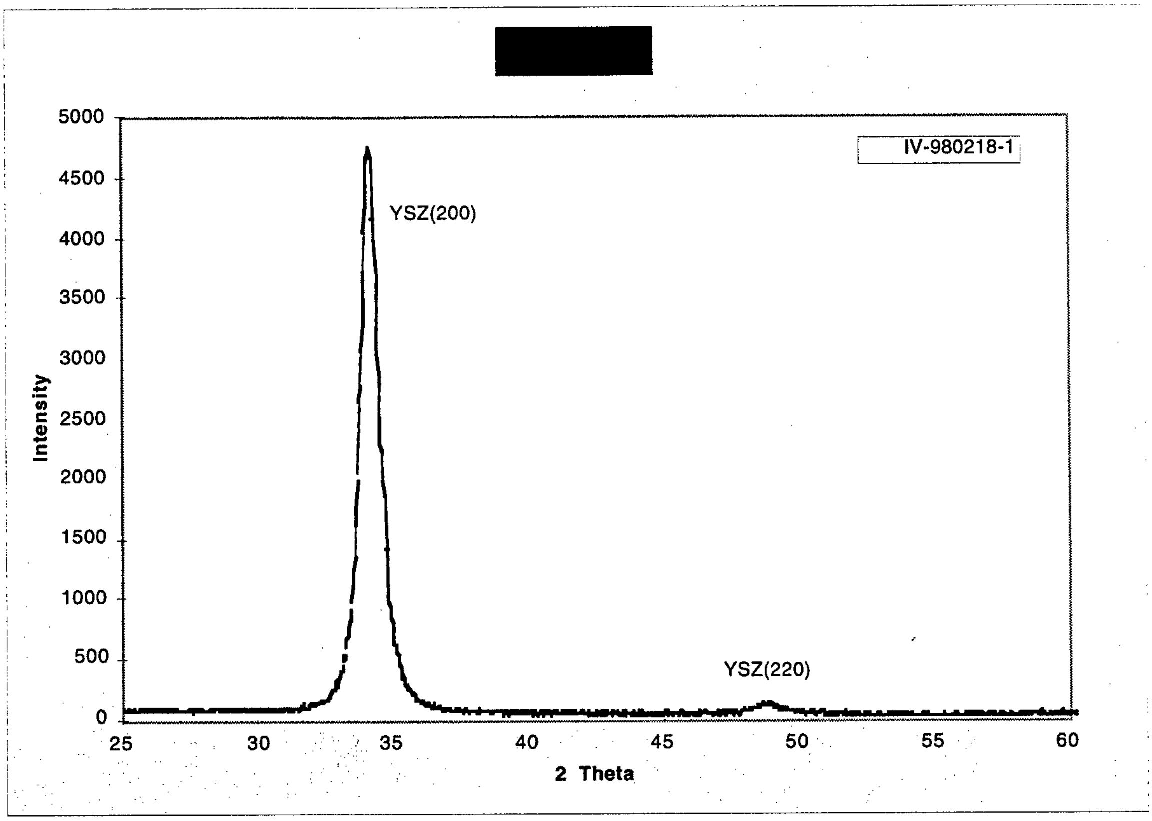


Figure 14: XRD of 0.5 um YSZ film as deposited

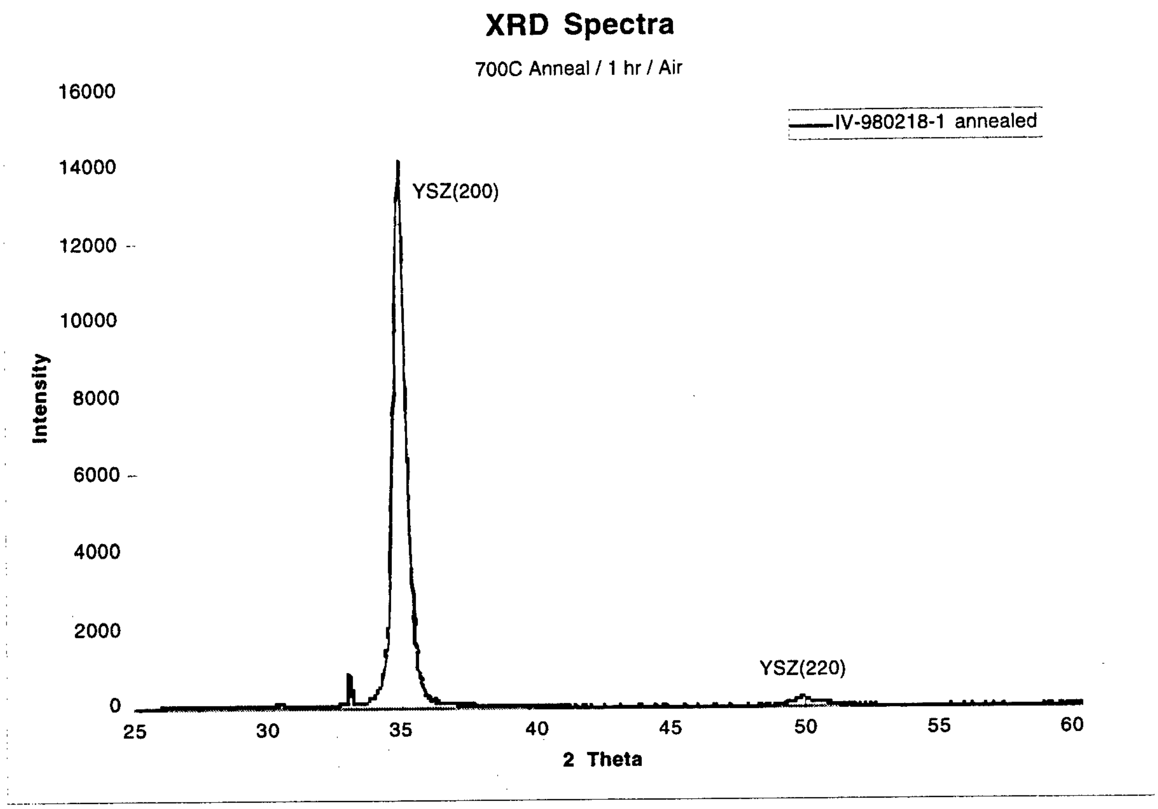


Figure 15: XRD spectra of same film after annealing to 700C for 1 hr in air.

The other key aspect of this growth is the need for in-plane orientation. YSZ phi scans measure the degree of in plane orientation of the YSZ polycrystals by measuring the orientation of a diffracted XRD peak which lies in the plane of the film. The spread of the peak is a measure of the degree of alignment of all the polycrystals. A well behaved film with cubic symmetry will have 4 peaks 90 degrees apart in a 360 degree rotation with a few degree FWHM spread in the peak width. The thin films that we have fabricated on silicon nitride (Figure 16) have been measured by the Los Alamos National Laboratory Superconducting Material Group and display 4 peaks showing that there is some modest in-plane alignment. The peak widths, a measure of the crystallite alignment, still remain wider than desired.

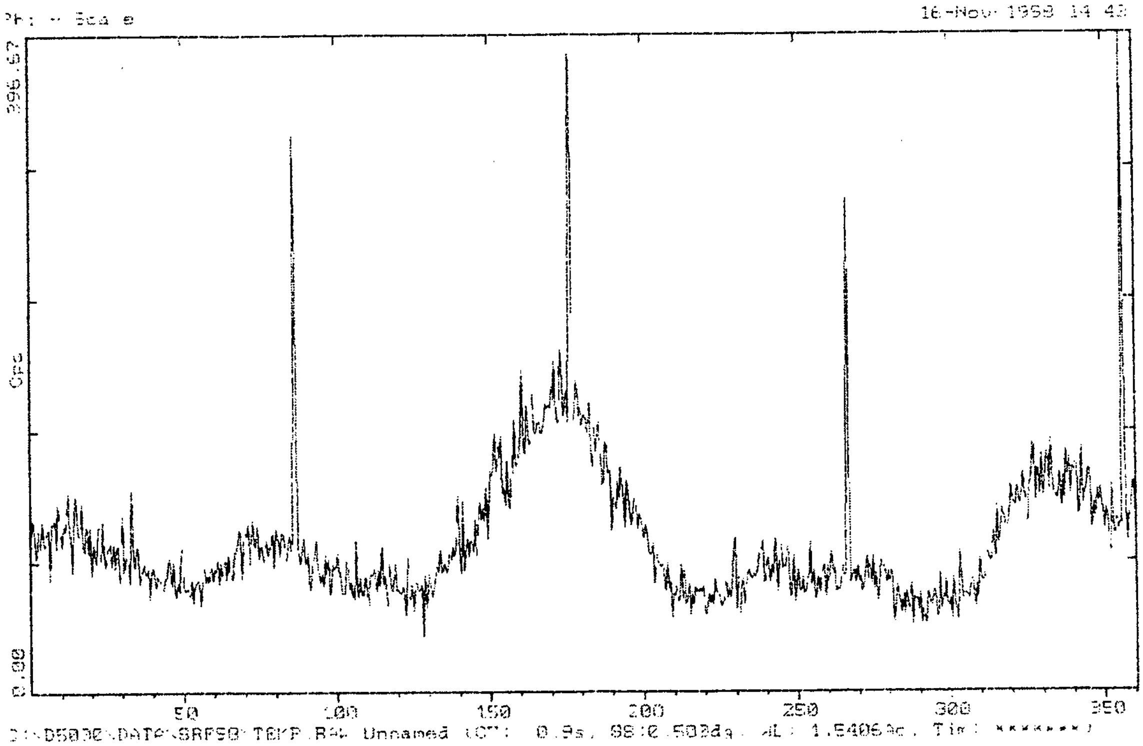


Figure 16: Phi Scan of YSZ film on Si_3N_4

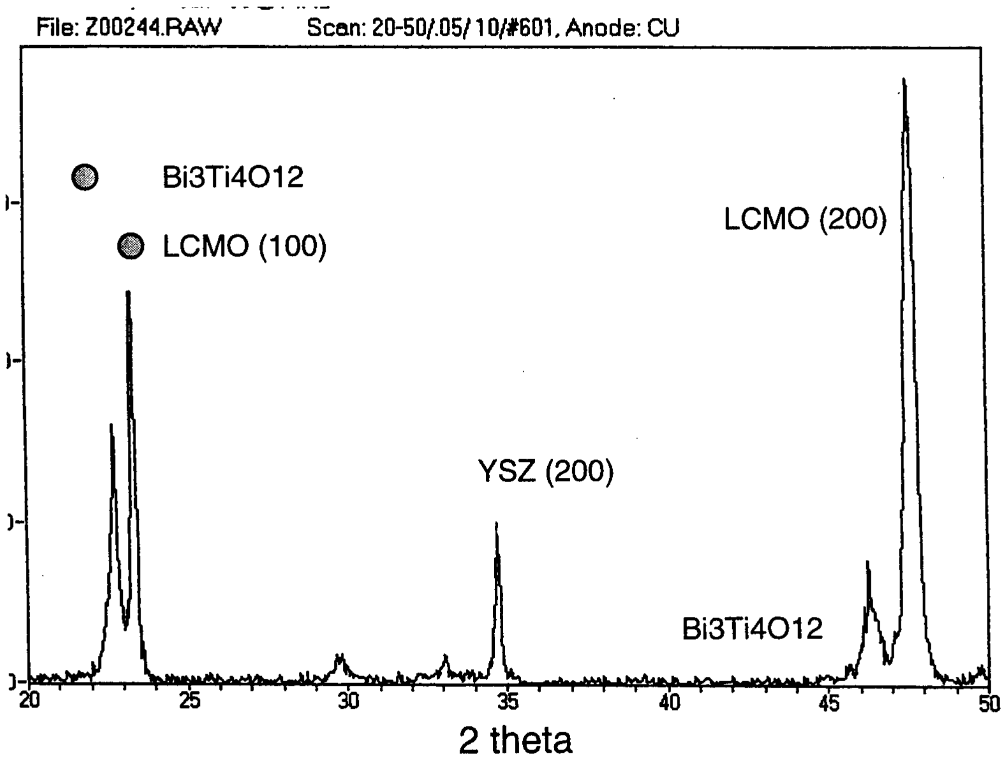


Figure 17: Growth of LCMO/$Bi_3TI_4O_{12}$/YSZ on Si_3N_4 coated Si.

The additional buffer films of $Bi_3Ti_4O_{12}$ and the LCMO resistor material have the proper out-of-plane oriented growth as desired when deposited on this YSZ buffer film as shown in Figure 17. LCMO films deposited on these first YSZ/Si_3N_4 films have exhibited TCRs of 3.5 % at a TCR transition temperature of -40C as shown in Figure 18.

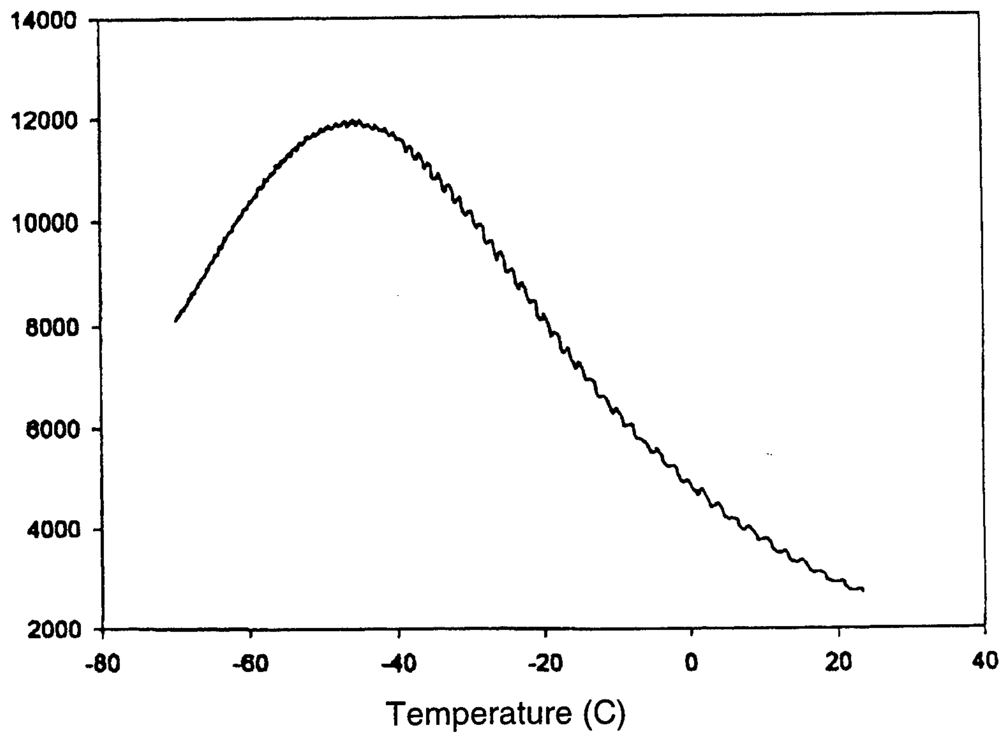


Figure 18: Resistance properties of first bolometer films on YSZ.

Summary

We have demonstrated that oriented YSZ buffer films can be deposited on Si_3N_4 coated Si wafers, the fundamental support structure for bolometer pixels. These buffer films have subsequently been used to grow oriented LCMO CMR films which have demonstrated high TCR. Further work is ongoing to further refine and improve the film properties, a first step in the demonstration of pixels and arrays with improved infrared sensitivity.